

An Operational Supramolecular Nanovalve

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The advent of supramolecular chemistry¹ has equipped chemists with the synthetic knowledge to construct molecule-level machines^{2,3} using template-directed protocols.⁴ The concept of nanoscopic machines has been realized in solution,^{2,3} at air–water interfaces,⁵ on surfaces,^{6,7} and in solid-state devices.⁸ At a supramolecular level, in complexes we have called⁹ pseudorotaxanes, the self-assembly of the components can be reversed upon quelling temporarily the molecular recognition that exists between matching pieces. Thus, a supramolecular machine can be defined⁶ as an assembly of two or more molecular components designed to perform mechanical-like motions in response to stimuli—which include^{2,3} chemical, electrochemical, and photochemical pulses—that can be switched on and off at will. In [2]pseudorotaxanes, the dethreading and rethreading movements of the rod from the ring component are reminiscent² of the motions of a linear motor. There are a number of artificial supramolecular machines^{2,3} based on [2]pseudorotaxanes that can be induced to undergo co-conformational changes¹⁰ by chemical, electrochemical, or photochemical means.

Although it has been demonstrated^{2,3} that pseudorotaxanes thread and dethread in solution, to do useful work and hence realize their potential as machines, they have to be attached to solid supports. Previously, we have shown⁶ that photochemically induced threading and dethreading of a pseudorotaxane-based machine does occur when it is attached to a silica surface. Here, we describe (i) the tethering of pseudorotaxanes as gates at the entrances of ~ 2 nm diameter, cylindrical pores¹¹ in mesostructured silica (ii) to create nanovalves (Figure 1) capable of trapping luminescent molecules and able (iii) to release them on demand.

The [2]pseudorotaxane [DNPDCBPQT]⁴⁺ was employed as a gatekeeper in the form⁶ of a tethered 1,5-dioxynaphthalene (DNP)-containing derivative (DNPD), acting as the gatepost, and cyclobis-

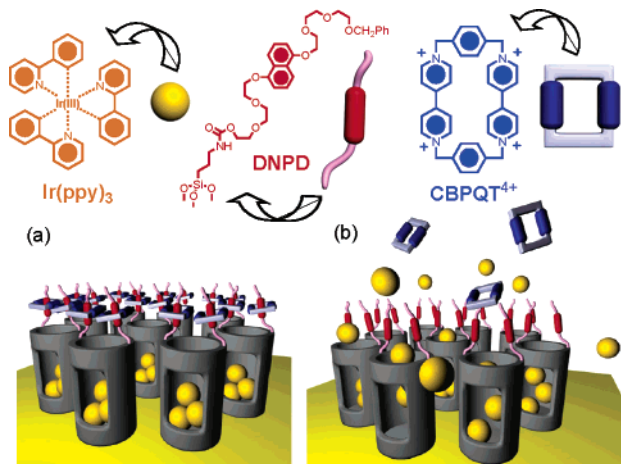


Figure 1. Graphical representations of operation of nanovalves. (a) The orifices of the nanopores (diameter 2 nm) are covered with pseudorotaxanes (formed between DNPD and CBPQT⁴⁺) which trap the luminescent Ir(ppy)₃ molecules inside the nanopores. (b) Upon their reduction, the CBPQT²⁺ bisradical dications are released and so allow the Ir(ppy)₃ to escape.

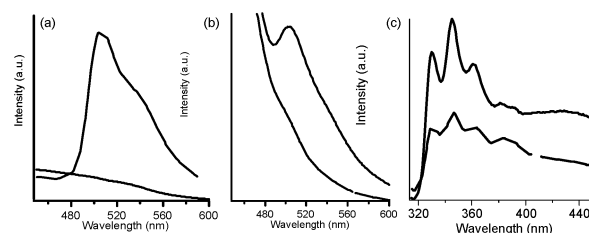


Figure 2. (a/b) Emission spectra of Ir(ppy)₃ excited at 380 nm. (a) Emission in film before (lower trace) and after (upper trace) opening valve. (b) Absence of emission in solution before (lower trace) and presence of emission after (upper trace) opening valve. (c) Emission of DNP attached to film surface. The low intensity (lower trace) corresponds to partial quenching of emission by CBPQT⁴⁺. On opening the valve, the original intensity (upper trace) is restored.

(paraquat-*p*-phenylene) (CBPQT⁴⁺), which recognizes DNP units on account of a cooperative array of noncovalent interactions, serving as the gate that controls access in and out of the nanopores. By using tris(2,2′-phenylpyridyl)iridium(III),¹² Ir(ppy)₃—which has a diameter of ca. 1 nm and exhibits fluorescent emission at 506 nm—as the trapped molecules, the release process from the nanopores can be followed by fluorescence spectroscopy. The power supply¹³ is an external reducing reagent (NaCNBH₃) that opens the nanovalve and allows the release of the luminescent molecules. The operation of the nanovalve involves four stages: (i) preparing the container, (ii) filling it, (iii) closing the valve, and (iv) opening the valve to release its contents.

The first steps in preparing the nanovalve are making the nanocontainer with gateposts, before filling it with fluorescent molecules and closing the gate. A sol–gel-based dip-coating method was used to effect the rapid synthesis of continuous mesostructured thin films consisting¹⁴ of a 2-D hexagonal array. Calcination produced the hexagonal array of empty pores. The films were supported by a silicon substrate and the pore openings—in addition to the remainder of the film’s surface—were derivatized (Figure 1) with the linear components, i.e., the DNPD gateposts. The pores were diffusion-filled with Ir(ppy)₃ by immersing the films in a 1.0 mM PhMe solution. The gate was then closed by placing the film in an aqueous 1.0 mM solution of CBPQT⁴⁺Cl, allowing the DNPD tethers to be threaded by the bulky CBPQT⁴⁺ (ca. 0.8 × 1.0 nm) tetracations which block the pore openings. The emission at 506 nm from the film indicates (Figure 2a) that the Ir(ppy)₃ is inside the containers and the decreases (Figure 2c) in the emission at 330, 345, and 360 nm from the DNP units allow us to monitor when CBPQT⁴⁺ tetracations are threaded and the containers are blocked.

The next step was to operate the nanovalve. The film containing the pores with closed valves was placed in a cuvette which contained PhMe/EtOH (1:1), and the luminescence intensity of the released Ir(ppy)₃ was monitored¹⁵ over time (Figure 3a). After a few minutes, NaCNBH₃ was added¹⁶ to the mixed solvent and a sudden jump in intensity was observed, indicating that the valve has opened—i.e., the pseudorotaxane has disassembled—and the Ir-

(ppy)₃ has been released from the container into the surrounding solvent. To verify that the operation of the valve involves dethreading of CBPQT⁴⁺, films that were not exposed to the tetracations (and thus contain open pores) were studied. As soon as the film was placed in solution, the iridium complex escaped from the pores and a sudden jump in intensity was observed (Figure 3b), i.e., when the gate is not closed, Ir(ppy)₃ is lost immediately. After the valve had opened and dethreading had occurred, the emission spectra of the film and solution were recorded. The solution was found (Figure 2b) to have an emission band at 506 nm because of the presence of the released Ir(ppy)₃ and the 506 nm band originally observed in the film disappeared (Figure 2a). The intensity of the emission of the DNPd attached to the film at the pore openings increased (Figure 2c) since CBPQT⁴⁺ is no longer quenching the emission.

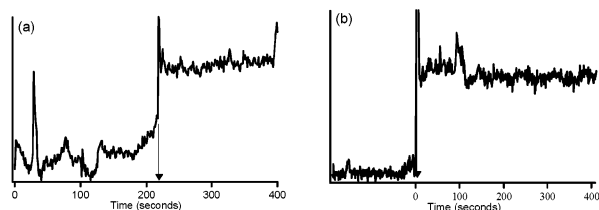


Figure 3. Luminescence intensity of Ir(ppy)₃ in solution during valve operation. (a) Film with valves closed is inserted into the solution at $t = 0$ s. The reducing agent is added at 218 s, as indicated by the arrows. The immediate increase in intensity heralds the release of the trapped Ir(ppy)₃ molecules into solution. (b) Film without valves is added at $t = 0$ s. The immediate rise in intensity signifies that Ir(ppy)₃ has escaped.

We have demonstrated a functioning molecular machine, namely a supramolecular nanovalve that opens and closes the orifices around nanopores which accept and release small numbers of molecules on demand. The nanopores are created using a one-step, one-pot, dip-coating technique. They can be filled with guest molecules and trapped by redox-controlled, gate-keeping supermolecules. An external reducing reagent can be used to break up the supermolecules, allowing the release of the guest molecules. Future applications could involve the trapping and release of other molecules such as drugs and enzymes. Electrical and photochemical energy could also be used to power the nanomachinery. This operational supramolecular nanovalve is a true molecular machine,¹⁷ consisting of a solid framework with movable parts capable of doing work. In Feynman's famous quote, "there's plenty of room at the bottom", he alludes¹⁸ to the potential use of atoms and molecules in devices and machines on the nanometer scale. The nanovalve controls access to the room at the bottom.

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- (15) X-ray diffraction (XRD) patterns of the films were taken before and after the threading experiments to verify that release of the Ir(ppy)₃ molecules was not caused by destruction of the containers. Both XRD patterns contained peaks at the same values of 2θ .
- (16) To verify that the external reducing agent does not affect the luminescence intensity of dissolved Ir(ppy)₃ and thus produce a false indication of release, the luminescence intensity was observed after NaCNBH₃ was added to the solution, proving that the external reducing agent does not affect the luminescence properties of the iridium complex. Spectra were taken using a fluorolog spectrophotometer and a photon counter.
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